Direct capture of low-concentration CO_2 and selective hydrogenation to CH_4 over Al_2O_3-supported Ni-La dual functional materials

Tomotaka Tatsumichi[a], Rei Okuno[a], Hideki Hashimoto[a,b], Norikazu Namiki[a], Zen Maeno[a,*]

[a]School of Advanced Engineering, Kogakuin University, 2665-1, Nakano-machi, Hachioji, Tokyo, 192-0015, Japan

[b]Center for Basic Research on Materials, National Institute for Materials, Science, 1-2-1, Sengen, Tsukuba, Ibaraki 305-0047, Japan, PRESTO, Japan Science and Technology Agency (JST), Kawaguchi, Saitama, 332-0012, Japan

*Corresponding author

Zen Maeno, E-mail: zmaeno@cc.kogakuin.ac.jp

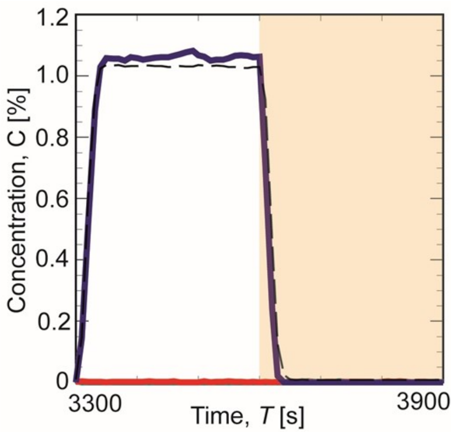

Figure S1. Comparison of CO_2 profiles in blank tests with SiC (blue solid line) and without any material (black dashed line).

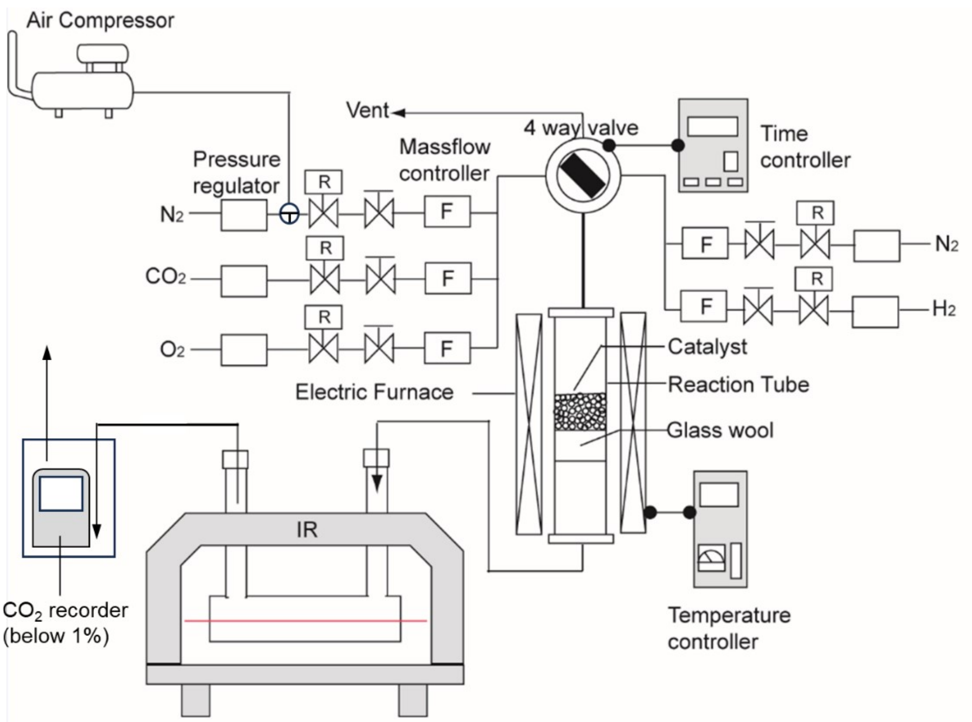

Figure S2 Schematic view of reactor setup of CCR including gas detector system.

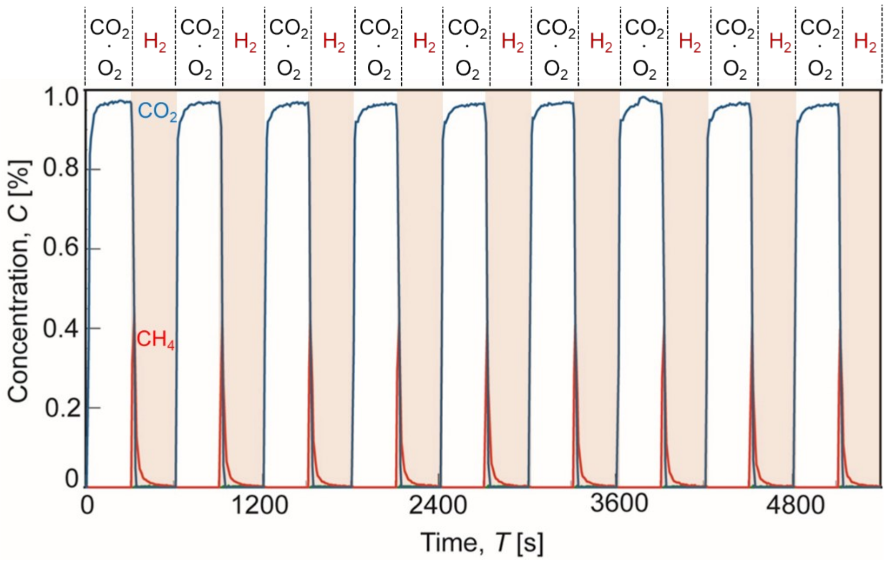

Figure S3 Concentration profile of CO_2 and CH_4 in CO_2 capture in the presence of O_2 and hydrogenation using Ni-La(15)/Al_2O_3.

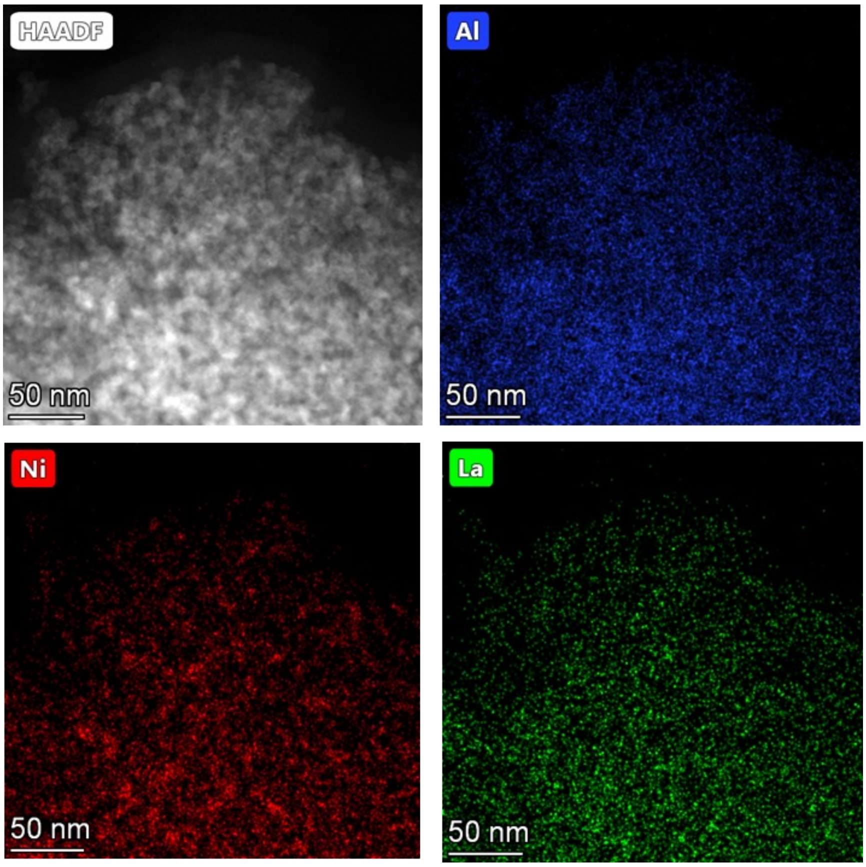

Figure S4 Different HAADF-STEM image and elemental mapping obtained by EDX spectroscopy for Ni-La(15)/Al_2O_3

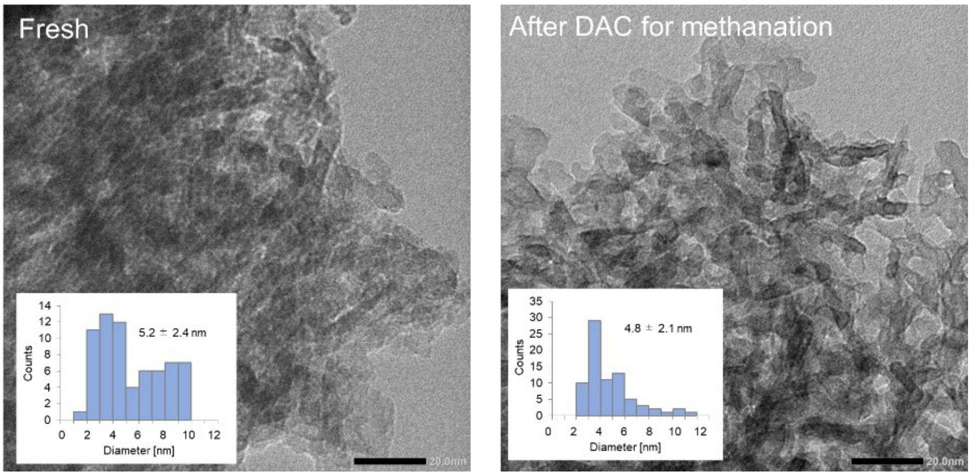

Figure S5 TEM images of fresh and spent Ni-La(15)/Al_2O_3 (after 80 cycles of DAC and methanation)

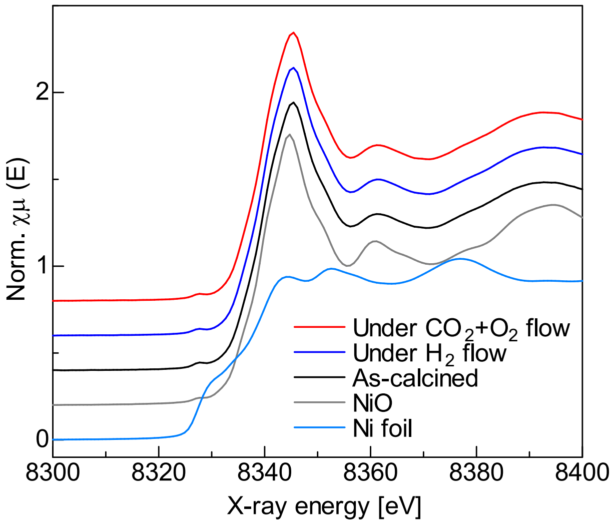

Figure S6 Ni K-edge XANES spectra of Ni-La(15)/Al_2O_3 before CCR (as-calcined), after H_2 pretreatment (under H_2 flow), and during CO_2 capture from the mixture with O_2 (under CO_2+O_2 flow). The spectra of Ni-La(15)/Al_2O_3 were recorded at 350 C using an in situ quartz cell connecting to gas mixture systems (at BL14B2 in SPring-8) without exposure to air whereas two reference samples were measured at ambient temperature.

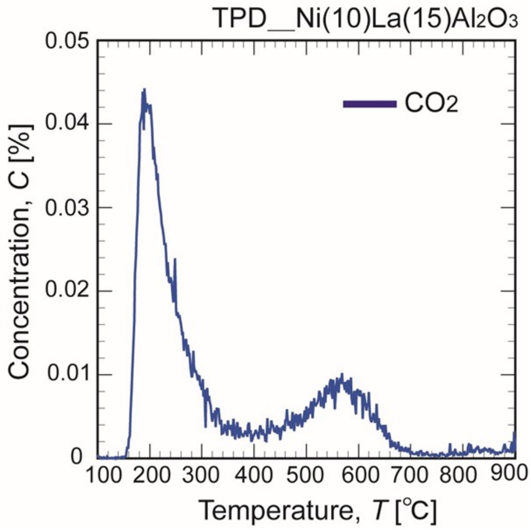

Figure S7 TPD profile of CO_2-preadsorbed Ni-La(15)/Al_2O_3. The H_2 prereduced DFMs were exposed to 1% CO_2+20% O_2/N_2 flow at 100 °C, followed by N_2 purge for 15 min and successive TPD measurement under N_2 flow with increasing the temperture to 600 °C (10 °C /min).

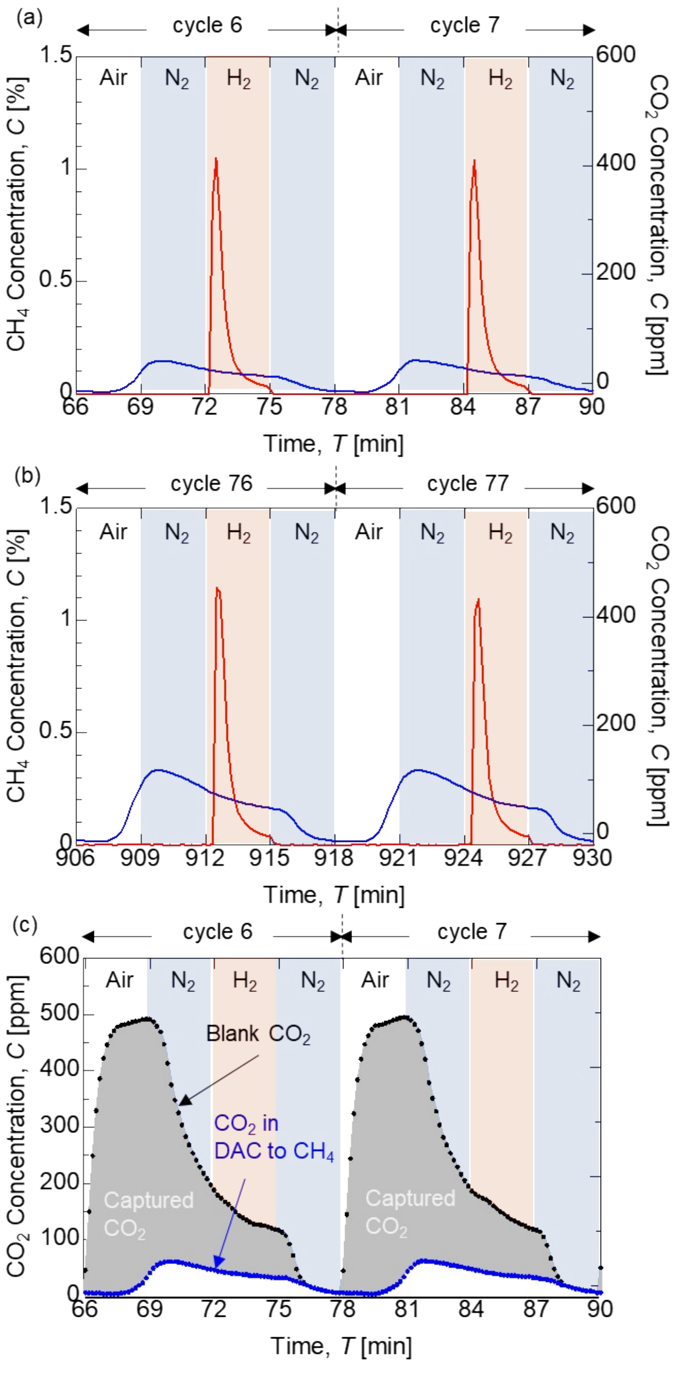

Figure S8 (a and b) Concentration profile of CO_2 (red) and CH_4 (blue) in ambient DAC and methanation using Ni-La(15)/Al_2O_3 in different cycles. (c) Comparison of CO_2 concentration profile with blank test (black dot line).

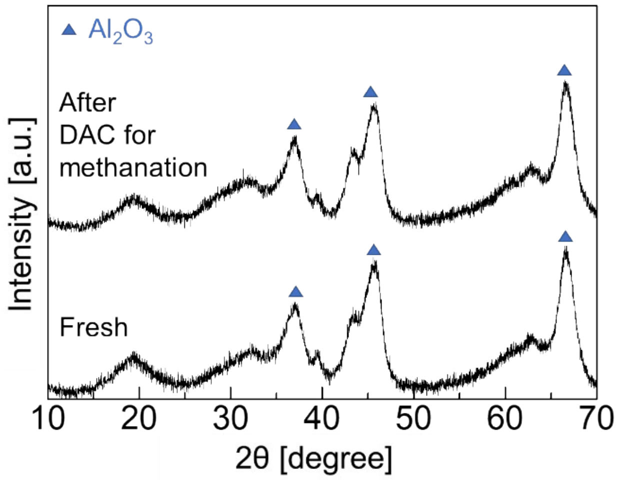

Figure S9 XRD patterns of fresh and spent Ni-La(15)/Al_2O_3.

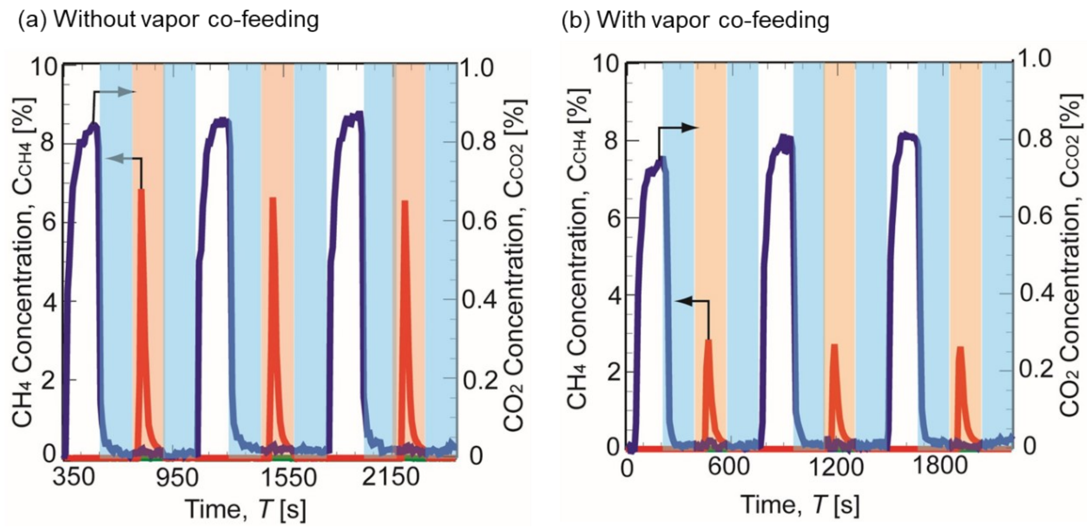

Figure S10 Concentration profile of CO_2 and CH_4 in CCR with or without vapor co-feeding.

Table S1 Results of CCR test over a series of Ni-based DFMs in the absence of O_2

DFM	Ad_{CO2} [a] [mmol/g]	Q_{CH4} [a] [mmol/g]	C_{CH4_Max} [b] [ppm]	S_{CH4} [c] [%]	$Conv_{adCO2}$ [c] [%]
Ni-La(15)/Al_2O_3	0.158	0.120	7798	99	76
Ni-Ca(4)/Al_2O_3	0.129	0.121	4938	93	94
Ni-Na(3)/Al_2O_3	0.219	0.173	9006	94	82

Reaction conditions: 0.1 g of catalyst, 350 °C, 100 mL/min of 1% CO_2/N_2 for 5 min, followed by 100 mL/min 20% H_2 /N_2 for 5 min. b Composition of the effluent gas at the outlet was quantitatively analysed using FTIR spectroscopy combined with a gas cell. c Based on the amount of CO and CH_4 generated during the reduction period.

Table S2 Comparison of CH_4 formation amount among reported DFMs under mild reaction conditions in the co-presence of O_2

DFM	Adsorption conditions	Hydrogenation conditions	CH_4 formation [mmol/g]	Ref.
Ni-La(15)/Al_2O_3	1% CO_2+20% O_2/N_2, 350 °C, 5 min	20% H_2/N_2, 350 °C, 5 min	0.129	This work
5% Ru 10% CaO/γ-Al_2O_3	10% CO_2/Air, 320 °C, 20 min	5% H_2/N_2, 320 °C, 20 min	0.50	[S1]
15NiCa/Al_2O_3	10% CO_2/Air, 360 °C, 1 min	10% H_2/Ar, 360 °C, 2 min	0.109	[S2]
Na_2O-Ni/Al_2O_3	7.5% CO_2+4.5% O_2+ 15% H_2O/N_2, 320 °C, 20 min	15% H_2/N_2, 320 °C, >20 min	0	[S3]

Reference [S1] *Appl. Catal. B*, **2015**, *168-169*, 370. [S2] *J. CO2 Util.*, **2019**, *34*, 576. [S3] *Chem. Eng. J.*, **2019**, *375*, 121953.

Table S3 Results of CCR over Ni-La(15)/Al_2O_3 with or without vapor co-feeding

Condition	Q_{CH4} [a] [mmol/g]	C_{CH4_Max} [b] [ppm]	S_{CH4} [c] [%]
With co-feeding (100 RH% at 25 °C)	0.076	66779	99
Without co-feeding	0.038	27429	99

Reaction conditions: 2 g of catalyst, 350 °C, 1000 mL/min of 0.8% CO_2+20% O_2/N_2 or 0.8% CO_2+20% O_2+vapor (100 RH% at 25 °C)/N_2 for 3 min, followed by 100 mL/min H_2 for 3 min. b Composition of the effluent gas at the outlet was quantitatively analysed using FTIR spectroscopy combined with a gas cell. c Based on the amount of CO and CH_4 generated during the reduction period.